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Visible Light-Induced Radical Rearrangement to Construct C−C Bonds via an Intramolecular Aryl Migration/Desulfonylation Process

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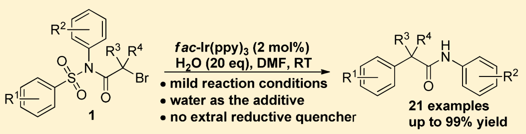
Ⓢ *Supporting Information*

ABSTRACT: A highly efficient intramolecular selective aryl migration/desulfonylation of 2-bromo-*N*-aryl-*N*-(arenesulfonyl)amide via visible light-induced photoredox catalysis has been accomplished. This approach allows for the construction of a variety of multisubstituted *N*,2-diarylacetamide under mild reaction conditions.

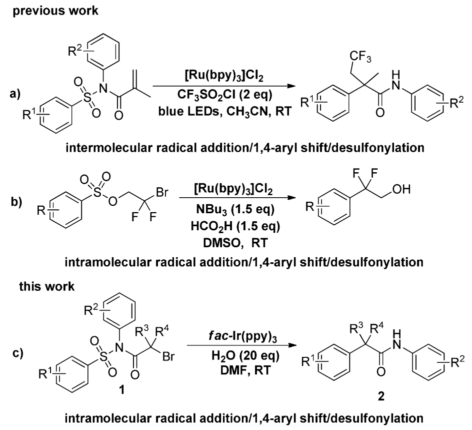


INTRODUCTION

Aryl migration reaction was considered as an efficient method to reconstruct complex compounds and had been widely applied to the synthesis of natural products.[1] Among them, the free radical aryl migrations can occur between carbon and carbon radicals and carbon and heteroatom-centered radicals to reconstruct the bond of C−X (X = C, Si, N). While in the early reports, poisonous radical initiator was usually used in the aryl migration reactions,[2,3] and a tremendous effort has been made to seek more efficient methods for this kind of reaction. Recently, Zhu's group reported an aryl migration reaction using 3 equiv of dicumyl peroxide as a radical initiator under the temperature of 140 °C to give desired products in good yields.[4] In addition, transition metal-mediated reactions have also been applied to the field of aryl migration reactions. For example, Nevado's group has reported a copper-catalyzed aryl migration reaction by using Togni's reagent[5] to generate trifluoromethyl radical species.[6] Although some progress has been made, these transformations still suffered the common drawbacks of harsh reaction conditions including high temperature, high catalyst loading, narrow range of substrates, and the use of poisonous or environment-unfriendly radical initiators.[7] Therefore, it is profound and significant to develop mild and effective methodologies for aryl migration reactions.

In recent years, visible light photoredox catalysis has received widespread attention as a powerful tool in the field of synthetic organic chemistry owing to its attractive features including mild reaction conditions, excellent functional group tolerance, and high reactivity.[8,9] To the best of our knowledge, several groups have reported intermolecular radical addition/1,2-aryl migration reaction via visible light-induced conditions.[10] However, few examples of intramolecular aryl migration reactions under the visible light-mediated condition have been reported until some works have been introduced by Xia's group and Stephenson's group.[11] Xia's group has reported a intermolecular radical addition/1,4-aryl shift/desulfonylation cascade reaction with a trifluoromethyl radical involved as the key radical source (Scheme 1a). On the other hand, Stephenson's group provided an efficient approach to achieve the benzylic difluoroethanol motif via an intramolecular radical addition/1,4-aryl shift/desulfonylation process (Scheme 1b). Besides that, the activation of C−X (X = Cl, Br, I) by visible-light participation has been widely reported in recent years,[12] and an efficient intramolecular dearomative cyclization reaction occurring via C−Br bond fragmentation has been reported by our group.[13] Therefore, we envisioned that 2-bromo-*N*-phenyl-*N*-(phenylsulfonyl)acetamide could generate *α*-carbonyl radical under visible light catalysis, which may then undergo intramolecular *ipso* addition/elimination and hydrogen abstraction followed by polar extrusion of SO_2 leading to the desired product. Herein, we report a visible light-induced intramolecular aryl migration/desulfonylation process for the

Scheme 1. Reported the Aryl Migration Reactions and Our Strategy



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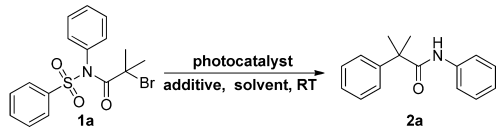
synthesis of *N*,2-diarylacetamide products under mild reaction conditions (Scheme 1c).

■ RESULTS AND DISCUSSION

We initiated our investigation by examining the reaction of 2-bromo-2-methyl-*N*-phenyl-*N*-(phenylsulfonyl)propanamide (**1a**) with *fac*-Ir(ppy)$_3$ (2 mol %) in DMF under a 23 W household fluorescent lamp irradiation (Table 1, entry 1). Fortunately, the reaction occurred at room temperature, giving the desired product (**2a**) with 26% yield. However, other photocatalysts, such as Ir(ppy)$_2$(bpy)PF$_6$, Ru(ppy)$_3$Cl$_2$, and Eosin Y do not work. Next, our attention was paid to screening the additives to improve the efficiency of the reaction.[14] When Li_2CO_3, Na_2CO_3, or $NaHCO_3$ was added, the reaction gave much higher yields (Table 1, entries 2−4); however, the byproducts (see Supporting Information) were also obtained. So we turned to use a weaker base like KH_2PO_4, a lower yield was observed without any byproducts (Table 1, entry 5). On the other hand, water was introduced as an additive because it could serve as a hydrogen donor in the reaction.[15] To our delight, the yield could be increased to 85% when 5 equiv of water was used as the additive (Table 1, entry 6). By increasing the amount of water to 20 equiv, a significantly increase of yield was observed and an 88% isolated yield was obtained (Table 1, entry 7). There is no influence on the yield when the amount of water was further increased (Table 1, entry 8). We then screened the solvents in the presence of water as the additive. Among solvents tested, DMF was proved to be the best choice for this reaction (Table 1, entries 9−12). The control experiments showed that both photocatalyst and visible light were essential for this reaction. When the reactions were conducted without catalyst or visible light, no product was formed (Table 1, entries 13 and 14).

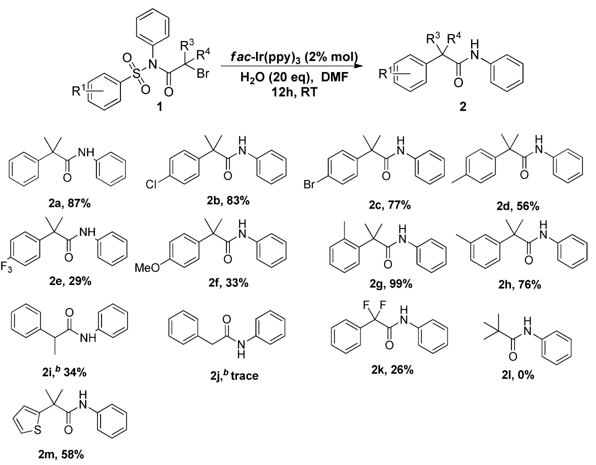
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst (2% mol)	addition (equiv)	solvent	conversion (%)	yield[b] (%)
1	*fac*-Ir(ppy)$_3$		DMF	36	26
2	*fac*-Ir(ppy)$_3$	Li_2CO_3 (1)	DMF	88	50
3	*fac*-Ir(ppy)$_3$	Na_2CO_3 (1)	DMF	100	63
4	*fac*-Ir(ppy)$_3$	$NaHCO_3$ (1)	DMF	88	40
5	*fac*-Ir(ppy)$_3$	KH_2PO_4 (1)	DMF	53	43
6	*fac*-Ir(ppy)$_3$	H_2O (5)	DMF	100	85
7	*fac*-Ir(ppy)$_3$	H_2O (20)	DMF	100	93 (88)[c]
8	*fac*-Ir(ppy)$_3$	H_2O (50)	DMF	100	93
9	*fac*-Ir(ppy)$_3$	H_2O (20)	DMA	85	72
10	*fac*-Ir(ppy)$_3$	H_2O (20)	CH_3CN	57	52
11	*fac*-Ir(ppy)$_3$	H_2O (20)	DCM	50	43
12	*fac*-Ir(ppy)$_3$	H_2O (20)	MeOH	<5	trace
13[d]	*fac*-Ir(ppy)$_3$	H_2O (20)	DMF	0	0
14		H_2O (20)	DMF	0	0

[a]Reaction conditions: **1a** (0.25 mmol), catalyst (2% mol), addition solvent (2.5 mL), rt, 12 h, under N_2 atmosphere. [b]Determined by ^{1}H NMR analysis with 4,4′-di*tert*-butyl-1,1′-biphenyl as an internal standard. [c]The value in parentheses was isolated yield. [d]In the dark.

Table 2. Substrate Scope of Substituted Sulfonyl Groups and *α*-Bromoacetamide[a]

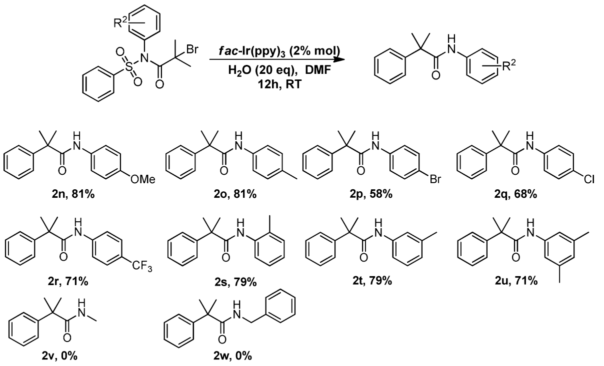


[a]Standard conditions: **1** (0.25 mmol), catalyst (2% mol), water (5 mmol), solvent (2 mL), rt, 12 h, under N_2 atmosphere. Isolated yields are provided. [b]1 equiv of Li_2CO_3 was added instead of water.

With the optimized reaction conditions in hand, we studied the substrate scope of this reaction. As shown in Table 2, a variety of substituted substrates, including methyl and halogen groups on the para-position of the N-phenyl (SO_2) ring, were compatible under the optimized reaction conditions, providing the desired products in good yields (Table 2, **2a**−**2d**). Substrates with strong electron-withdrawing group (trifluoromethyl) on the *N*-phenyl (SO_2) ring at the *para*-position gave the desired products **2e** in 29% yield and a byproduct (2-bromo-2-methyl-*N*-phenylpropanamide) was obtained with 30% yield. When the phenyl ring was functionalized with strong electron-donating groups, such as a methoxy group, a lower yield of the desired product **2f** was obtained and some of the starting material remained unchanged. It is worth noting that a minor steric hindrance did not impose any negative effect on yield; on the contrary, a better migration ability led to a better yield. As a result, when 2-bromo-2-methyl-*N*-phenyl-*N*-(*o*-toluenesulfonyl)propanamide (**1g**) was introduced, a quantitative yield of product **2g** could be afforded, in contrast to the substrate 2-bromo-2-methyl-*N*-phenyl-*N*-(*m*-toluenesulfonyl)propanamide(**1h**), which gave the desired product **2h** in 76% yield. The substrate with methyl group on the *N*-phenyl (SO_2) ring at the meta-position gave the desired products **2h** in 76%. In addition, when the standard reaction condition was applied to substrates with only one *α*-methyl substituent or no substituent on the carbonyl, no products (**2i**, **2j**) were observed, this might be ascribed to the instability of the formed radical intermediate. As shown in Table 1, the conversion could be increased with the added base. Using 1 equiv of Li_2CO_3 instead of water, the desired product **2i** was obtained in 34% yield. However, under the same reaction conditions for **1i**, no product was obtained for substrate **1j**. When 2,2-difluoro-*N*,2-diphenylacetamide was introduced in this reaction, the desired product **2k** could be obtained with 26% yield. Finally, the product **2m** could be obtained in 58% yield when the heterocyclic substrate **1m** was introduced. However, the reaction did not work when the arenesulfonyl was replaced by an alkyl sulfonyl group (**2l**) in the presence of either water or lithium carbonate. This might be ascribed to the lower migration nature of methyl than phenyl.

Subsequently, different substituent groups on the aryl ring of amides were also examined as shown in Table 3. Amides with electron-donating groups on the phenyl ring, such as methyl, methoxy group, gave the desired products in high yields (Table 3, **2n**, **2o**). When the phenyl ring was functionalized with electron-withdrawing groups, such as Cl, Br, or CF_3, high yields of the desired products were also obtained (Table 3, **2p**, **2r**). Besides, as shown in Table 3, the steric hindrance of the substituents has little effect on the reaction. Thus, the product **2s** could be obtained from its corresponding starting material with good yields, and the position of substituents on the aryl ring of amides has little effect on the reaction (Table 3, **2o**, **2s**–**2u**). None of desired product **2v** or **2w** was obtained when the N-phenyl group was replaced by an N-alkyl group.

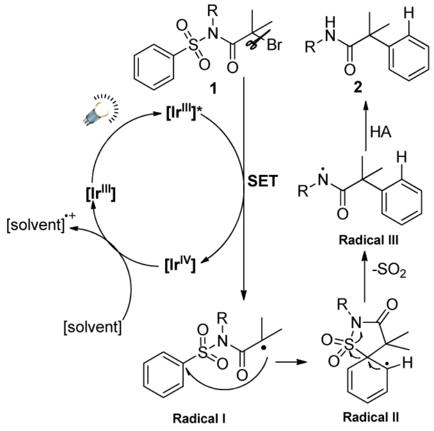
Table 3. Substrate Scope of Substituted Amides[a]



[a]Standard conditions: 2-bromo-*N*-phenyl-*N*-(phenylsulfonyl) propanamide (0.25 mmol), catalyst (2% mol), water (5 mmol), solvent (2 mL), rt, 12 h, under N_2 atmosphere. Isolated yields are provided.

On the basis of the above results, a plausible mechanism was proposed to account for this visible light-induced aryl migration reaction (Scheme 2). First, the iridium catalyst was excited to *fac-[Ir(ppy)$_3$] species under visible light irradiation, then it underwent a single electron transfer process with **1** to afford an α-alkyl radical intermediate **I** and Ir^{IV} metal complex (which may be reduced by the solvent).[11a,16] A 5-*ipso* cyclization then took place on the sulfonyl aromatic ring, generating aryl radical **II**, which would undergo rapid desulfonylation to form the key amidyl radical **III**. The amidyl radical **III** could undergo hydrogen abstraction (HA) from the solvent or water to give amides **2** as the target product.

Scheme 2. Proposed Mechanism of Aryl Migrations Reaction



CONCLUSION

In summary, an efficient visible light-induced aryl migration/desulfonylation reaction has been developed to form multi-substituted *N*,2-diarylacetamides. This photocatalytic approach provided a novel access to reconstruct complex compounds characterized by its operational simplicity and high yields under mild conditions. The application of visible light-induced method and the concept of aryl migration to construct useful molecules is ongoing in our lab.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Commercially available reagents were used without further purification. Anhydrous DMF, DMA, CH_3CN, DCM were freshly distilled from calcium hydride. Anhydrous MeOH was distilled over magnesium under nitrogen. ^{1}HNMR spectra were recorded at 400 MHz with TMS as an internal standard. ^{13}C NMR spectra were recorded at 100 MHz and referenced to the central peak of 77.00 ppm for $CDCl_3$. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. ^{19}F NMR was recorded at 376 MHz using CF_3COOH as an external standard. Mass spectroscopy data were collected on an HRMS-ESI of Q-TOF mass spectrometer. Irradiation of photochemical reactions was carried out using a 23 W household compact fluorescent lamp. Flash column chromatography was performed on silica gel (300–400 mesh) with petroleum (bp 60–90 °C) and the indicated solvent, which are listed below as volume/volume ratios.

Typical Procedure for the Preparation of 1a–1u, 1w.[17] A mixture of aniline (10.0 mmol) and triethylamine (10.0 mmol) in DCM (20.0 mL), sulfonyl chlorides (10.0 mmol) in DCM (10.0 mL) was added dropwise over a period of 1 h and stirred at room temperature for 6–10 h. After completion, the reaction was quenched with a 5% sodium carbonate solution (20.0 mL). Then the solution was transferred into the separating funnel, the organic phase was washed twice with water (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure to afford the corresponding secondary sulfonamide, which was used to the next reaction without further purification.

To a solution of the crude sulfonamide in DCM (20.0 mL) and ^{i}Pr$_2$NEt (12.0 mmol), 2-bromo-2-methylpropionyl bromide (12.0 mmol) was added dropwise slowly at room temperature in 3 h and stirred at room temperature for 6–10 h. After completion, the reaction was quenched with H_2O (20.0 mL) and extracted with DCM (3 × 25.0 mL). The combined organic extracts were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by recrystallization to give 2-bromo-*N*-aryl-*N*-(arenesulfonyl)amide.

*2-Bromo-2-methyl-N-phenyl-N-(phenylsulfonyl)propanamide **(1a)**.* White solid, 3.1 g; 81% yield; mp, 153.3–155.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.96 (m, 2H), 7.68–7.62 (m, 2H), 7.56–7.40 (m, 7H), 1.63 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.4, 138.1, 135.3, 133.8, 131.7, 130.4, 129.4, 128.9, 128.6, 58.3, 32.3. HRMS-ESI (m/z): calculated for $C_{16}H_{16}{}^{79}BrNNaO_3S$ $(M + Na)^+$, 403.9932; found, 403.9931.

*2-Bromo-N-(4-chlorophenyl)sulfonyl)-2-methyl-N-phenylpropanamide **(1b)**.* White solid, 3.4 g; 56% yield; mp, 127.2–128.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.85 (m, 2H), 7.56–7.37 (m, 7H), 1.63 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.7, 140.5, 136.4, 135.2, 131.6, 130.9, 130.5, 129.1, 128.9, 58.2, 32.3 HRMS-ESI (m/z): calculated for $C_{16}H_{16}{}^{79}BrClNO_3S$ $(M + H)^+$, 415.9723; found, 415.9705.

*2-Bromo-N-((4-bromophenyl)sulfonyl)-2-methyl-N-phenylpropanamide **(1c)**.* White solid, 1.7 g; 37% yield; mp, 126.6–128.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.77 (m, 2H), 7.72–7.63 (m, 2H), 7.54−7.36 (m, 5H), 1.64 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.7, 137.0, 135.1, 131.9, 131.6, 131.0, 130.5, 129.2, 129.1, 58.2, 32.3. HRMS-ESI (m/z): calculated for $C_{16}H_{16}{}^{79}Br^{81}BrNO_3S$ (M + H)$^+$, 461.9197; found, 461.9188.

2-Bromo-2-methyl-N-phenyl-N-tosylpropanamide (**1d**). White solid, 3.4 g; 85% yield; mp, 131.3−133.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86−7.80 (m, 2H), 7.53−7.38 (m, 5H), 7.33−7.31 (m, 2H), 2.45 (s, 3H), 1.63 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.4, 144.9, 135.4, 135.1, 131.8, 130.3, 129.5, 129.2, 128.9, 58.4, 32.4, 21.7. HRMS-ESI (m/z): calculated for $C_{17}H_{19}{}^{79}BrNO_3S$ (M + H)$^+$, 396.0269; found, 396.0258.

2-Bromo-2-methyl-N-phenyl-N-((4-(trifluoromethyl)phenyl)-sulfonyl)propanamide (**1e**). White solid, 1.4 g; 31% yield; mp, 136.2−139.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08−8.06 (m, 2H), 7.81−7.79 (m, 2H), 7.54−7.40 (m, 5H), 1.64 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.9, 141.7, 135.1, 131.6, 130.7, 130.4 (q, J = 41.8 Hz), 130.0, 129.2, 125.8 (q, J = 3.6 Hz), 123.1 (q, J = 271.4 Hz), 58.1, 32.3. HRMS-ESI (m/z): calculated for $C_{17}H_{15}{}^{79}BrF_3NO_3S$ (M + H)$^+$, 449.9986; found, 449.9988.

2-Bromo-N-((4-methoxyphenyl)sulfonyl)-2-methyl-N-phenylpropanamide (**1f**). White solid, 3.3 g; 80% yield; mp, 154.8−156.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95−7.84 (m, 2H), 7.58−7.37 (m, 5H), 7.03−6.93 (m, 2H), 3.89 (s, 3H), 1.63 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.4, 163.8, 135.5, 131.8, 131.7, 130.2, 128.8, 113.7, 58.4, 55.6, 32.4. HRMS-ESI (m/z): calculated for $C_{17}H_{19}{}^{79}BrNO_4S$ (M + H)$^+$, 412.0218; found, 412.0208.

2-Bromo-2-methyl-N-phenyl-N-(o-tolylsulfonyl)propanamide (**1g**). White solid, 3.0 g; 75% yield; mp, 112.2−114.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 8.0 Hz, 1H), 7.62−7.56 (m, 2H), 7.55−7.45 (m, 4H), 7.38 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 2.67 (s, 3H), 1.59 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.2, 138.8, 137.0, 134.5, 133.6, 132.4, 132.0, 131.7, 130.5, 129.0, 126.1, 58.4, 32.3, 20.8. HRMS-ESI (m/z): calculated for $C_{17}H_{19}{}^{79}BrNO_3S$ (M + H)$^+$, 396.0269; found, 396.0263.

2-Bromo-2-methyl-N-phenyl-N-(m-tolylsulfonyl)propanamide (**1h**). White solid, 1.8 g; 75% yield; mp, 99.3−100.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.56−7.36 (m, 7H), 2.44 (s, 3H), 1.63 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.3, 138.7, 137.9, 135.3, 134.5, 131.7, 130.3, 129.6, 128.8, 128.4, 126.4, 58.4, 32.3, 21.3. HRMS-ESI (m/z): calculated for $C_{17}H_{19}{}^{79}BrNO_3S$ (M + H)$^+$, 396.0269; found, 396.0278.

2-Bromo-N-phenyl-N-(phenylsulfonyl)propanamide (**1i**). White solid, 3.1 g; 83% yield; mp, 128.6−131.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10−8.03 (m, 2H), 7.69 (m, 1H), 7.62−7.48 (m, 5H), 7.39 (m, 2H), 4.01 (q, J = 6.8 Hz, 1H), 1.66 (d, J = 6.8 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.9, 138.1, 134.8, 134.1, 130.5, 130.2, 129.8, 129.1, 128.8, 39.4, 20.8. HRMS-ESI (m/z): calculated for $C_{15}H_{15}{}^{79}BrNO_3S$ (M + H)$^+$, 367.9956; found, 367.9958.

2-Bromo-N-phenyl-N-(phenylsulfonyl)acetamide (**1j**). Brown solid, 3.1 g; 87% yield; mp, 122.8−124.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.7−8.05 (m, 2H), 7.73−7.66 (m, 1H), 7.61−7.49 (m, 6H), 7.38−7.31 (m, 2H), 3.62 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.3, 138.0, 135.1, 134.2, 130.6, 130.0, 129.9, 129.1, 128.8, 28.9. HRMS-ESI (m/z): calculated for $C_{14}H_{13}{}^{79}BrNO_3S$ (M + H)$^+$, 353.9800; found, 353.9803.

2-Bromo-2,2-difluoro-N-phenyl-N-(phenylsulfonyl)acetamide (**1k**). White solid, 2.5 g; 65% yield; mp, 165.8−167.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11−8.02 (m, 2H), 7.74 (m, 1H), 7.64−7.45 (m, 5H), 7.35 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 23.62. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.7 (t, J = 28.3 Hz), 137.1, 134.8, 133.1, 130.92, 130.89, 129.7, 129.2, 129.1, 110.4 (t, J = 317.0 Hz). HRMS-ESI (m/z): calculated for $C_{14}H_{11}{}^{79}BrF_2NO_3S$ (M + H)$^+$, 389.9611; found, 389.9594.

2-Bromo-2-methyl-N-(methylsulfonyl)-N-phenylpropanamide (**1l**). White solid, 2.5 g; 79% yield; mp, 110.7−111.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52−7.45 (m, 5H), 3.41 (s, 3H), 1.71 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 172.7, 134.9, 131.2, 130.4, 129.6, 129.1, 42.6, 40.7, 32.3. HRMS-ESI (m/z): calculated for $C_{11}H_{14}{}^{79}BrNO_3S$ (M + H)$^+$, 319.9956; found, 319.9926.

2-Bromo-2-methyl-N-phenyl-N-(thiophen-2-ylsulfonyl)-propanamide (**1m**). White solid, 2.5 g; 41% yield; mp, 130.5−132.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 3.6, 1.2 Hz, 1H), 7.72 (dd, J = 4.8, 1.2 Hz, 1H), 7.53−7.36 (m, 5H) 7.13 (dd, J = 4.8, 3.6 Hz, 1H), 1.68 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.0, 137.4, 136.2, 135.2, 134.5, 131.5, 130.5, 129.0, 127.0, 58.3, 32.4. HRMS-ESI (m/z): calculated for $C_{14}H_{15}{}^{79}BrNO_3S_2$ (M + H)$^+$, 387.9677; found, 387.9674.

2-Bromo-N-(4-methoxyphenyl)-2-methyl-N-(phenylsulfonyl)-propanamide (**1n**). White solid, 3.6 g; 88% yield; mp, 168.7−170.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97−7.95 (m, 2H), 7.71−7.61 (m, 1H), 7.55−7.51 (m, 2H), 7.38−7.28 (m, 2H), 7.04−6.89 (m, 2H), 3.87 (s, 3H), 1.65 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.5, 160.9, 138.1, 133.7, 133.0, 129.4, 128.6, 127.5, 114.0, 58.3, 55.5, 32.4. HRMS-ESI (m/z): calculated for $C_{17}H_{19}{}^{79}BrNO_4S$ (M + H)$^+$, 412.0218; found, 412.0218.

2-Bromo-2-methyl-N-(phenylsulfonyl)-N-(p-tolyl)propanamide (**1o**). White solid, 3.7 g; 94% yield; mp, 87.0−88.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00−7.92 (m, 2H), 7.65 (m, 1H), 7.53 (m, 2H), 7.29 (m, 4H), 2.43 (s, 3H), 1.63 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.4, 140.8, 138.2, 133.7, 132.6, 131.5, 129.6, 129.4, 128.6, 58.3, 32.4, 21.4. HRMS-ESI (m/z): calculated for $C_{17}H_{19}{}^{79}BrNO_3S$ (M + H)$^+$, 396.0269; found, 396.0263.

2-Bromo-N-(4-bromophenyl)-2-methyl-N-(phenylsulfonyl)-propanamide (**1p**). White solid, 2.4 g; 53% yield; mp, 174.2−177.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95−7.93 (m, 2H), 7.67 m, 1H), 7.62−7.51 (m, 4H), 7.33−7.28 (m, 2H), 1.67 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.1, 137.8, 134.4, 134.0, 133.3, 132.2, 129.4, 128.7, 124.8, 57.9, 32.3. HRMS-ESI (m/z): calculated for $C_{16}H_{16}{}^{79}Br^{81}BrNO_3S$ (M + H)$^+$, 461.9197; found, 461.9202.

2-Bromo-N-(4-chlorophenyl)-2-methyl-N-(phenylsulfonyl)-propanamide (**1q**). White solid, 2.3 g; 56% yield; mp, 156.2−160.5 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (m, 2H), 7.70−7.63 (m, 1H), 7.55 (m, 2H), 7.46−7.41 (m, 2H), 7.39−7.33 (m, 2H), 1.67 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.1, 137.8, 136.6, 134.0, 133.8, 133.0, 129.4, 129.2, 128.7, 57.9, 32.3. HRMS-ESI (m/z): calculated for $C_{16}H_{16}{}^{79}BrClNO_3S$ (M + H)$^+$, 415.9723; found, 415.9706.

2-Bromo-2-methyl-N-(phenylsulfonyl)-N-(4-(trifluoromethyl)-phenyl)propanamide (**1r**). White solid, 2.0 g; 45% yield; mp, 159.4−161.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95−7.92 (m, 2H), 7.76−7.65 (m, 3H), 7.56 (m, 4H), 1.67 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.3, 138.8, 137.8, 134.1, 132.2, 129.5, 128.9 (q, J = 63.9 Hz), 128.8, 126.1 (q, J = 3.6 Hz), 126.0, 123.4 (q, J = 270.9 Hz), 57.9, 32.3. HRMS-ESI (m/z): calculated for $C_{17}H_{16}{}^{79}BrF_3NO_3S$ (M + H)$^+$, 449.9986; found, 449.9983.

2-Bromo-2-methyl-N-(phenylsulfonyl)-N-(o-tolyl)propanamide (**1s**). White solid, 2.2 g; 55% yield; mp, 100.0−101.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06−8.03 (m, 2H), 7.70−7.63 (m, 1H), 7.56 (m, 2H), 7.41 (m, 2H), 7.36−7.26 (m, 2H), 2.43 (s, 3H), 1.74 (s, 3H), 1.45 (s, 3H).^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 170.8, 140.6, 138.6, 134.9, 134.0, 131.8, 131.6, 130.8, 129.8, 128.7, 126.5, 58.2, 33.3, 30.5, 19.4. HRMS-ESI (m/z): calculated for $C_{17}H_{19}{}^{79}BrNO_3S$ (M + H)$^+$, 396.0269; found, 396.0252

2-Bromo-2-methyl-N-(phenylsulfonyl)-N-(m-tolyl)propanamide (**1t**). White solid, 3.5 g; 89% yield; mp, 108.8−110.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99−7.93 (m, 2H), 7.69−7.62 (m, 1H), 7.58−7.50 (m, 2H), 7.33 (m, 2H), 7.29−7.26 (m, 1H), 7.24−7.18 (m, 1H), 2.40 (s, 3H), 1.62 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 171.3, 139.0, 138.1, 135.0, 133.7, 132.3, 131.1, 129.3, 128.6, 128.5, 58.4, 32.3, 21.2. HRMS-ESI (m/z): calculated for $C_{17}H_{19}{}^{79}BrNO_3S$ (M + H)$^+$, 396.0269; found, 396.0284.

2-Bromo-N-(3,5-dimethylphenyl)-2-methyl-N-(phenylsulfonyl)-propanamide (**1u**). White solid, 3.7 g; 90% yield; mp, 119.6−120.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00−7.93 (m, 2H), 7.69−7.61 (m, 1H), 7.58−7.47 (m, 2H), 7.13 (s, 1H), 7.04 (s, 2H), 2.35 (s, 3H), 1.61 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 138.7, 138.2, 134.8, 133.7, 132.0, 129.4, 129.2, 128.5, 58.5, 32.4. HRMS-ESI (m/z), calculated for $C_{18}H_{20}{}^{79}BrNO_3S$ (M + H)$^+$, 410.0426; found, 410.0414.

N-Benzyl-2-bromo-2-methyl-N-(phenylsulfonyl)propanamide (**1w**). White solid, 3.4 g; 85% yield; mp, 120.6−122.6 °C. ^{1}H NMR

(400 MHz, $CDCl_3$): δ 7.76−7.74 (m, 2H), 7.56 (m, 1H), 7.42 (m, 2H), 7.36−7.27 (m, 5H), 5.56 (s, 2H), 1.88 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.1, 138.7, 136.3, 133.5, 128.9, 128.6, 128.3, 127.6, 126.7, 57.0, 52.1, 32.0. HRMS-ESI (*m*/*z*): calculated for $C_{17}H_{19}{}^{79}BrNO_3S$ (M + H)$^+$, 396.0269; found, 396.0273.

Procedure for the Preparation of 1v.[18] A mixture of KOH (20.0 mmol) and $MeNH_2{\cdot}HCl$ (10.0 mmol) in H_2O (10 mL) was stirred at room temperature. DCM (10 mL) and arenesulfonyl chlorides (10.0 mmol) were added. After stirring for 1 h (the reaction was monitored by TLC), the reaction mixture was extracted with DCM and dried over anhydrous Na_2SO_4. The solvent was evaporated to afford the product, which was used in the next step without purification.

To a solution of the crude sulfonamide in DCM (20 mL) and $^iPr_2NEt$ (12 mmol), the 2-bromo-2-methylpropionyl bromide (12 mmol) was added dropwise slowly at room temperature for 3 h and stirred at room temperature for 6−10 h. After completion, the reaction was quenched with H_2O (20 mL) and extracted with DCM (3 × 25 mL). The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by recrystallization to give 2-bromo-2-methyl-*N*- phenyl-*N*-(phenylsulfonyl)propanamide (**1v**) as a white solid.

*2-Bromo-N,2-dimethyl-N-(phenylsulfonyl)propanamide (**1v**).* White solid, 2.2 g; 70% yield; mp, 83.2−84.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (m, 2H), 7.67−7.60 (m, 1H), 7.54 (m, 2H), 3.77 (s, 3H), 1.93 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.4, 138.8, 133.8, 128.9, 128.4, 6.4, 36.2, 31.4. HRMS-ESI (*m*/*z*): calculated for $C_{11}H_{15}{}^{79}BrNO_3S$ (M + H)$^+$, 319.9956; found, 319.9963.

General Procedure for *fac*-Ir(ppy)$_3$-Catalyzed Intramolecular Migration Reaction. A dried Schlenk tube equipped with a stirrer bar which was evacuated and backfilled with nitrogen was added to substrate **1** (0.25 mmol), *fac*-Ir(ppy)$_3$ (0.005 mmol), and H_2O (5 mmol). Then 2.5 mL of DMF was added into the reaction tube via a syringe. The reaction mixture was degassed by the freeze−pump−thaw method and then irradiated with a 23 W CFL (compact fluorescent light) (distance ∼5 cm) for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure. Then, the pure product was obtained by flash column chromatography (PE/DCM = 5:1) on silica gel.

*2-Methyl-N,2-diphenylpropanamide (**2a**).* White solid, 52.1 mg; 87% yield; mp, 96.2−98.0 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48−7.22 (m, 10H), 7.10−7.03 (s, 1H), 1.67 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.5, 144.5, 137.9, 128.9, 128.8, 127.3, 126.4, 124.0, 119.6, 48.0, 27.0. HRMS-ESI (*m*/*z*): calculated for $C_{16}H_{18}NO$ (M + H)$^+$, 240.1388; found, 240.1381.

*2-(4-Chlorophenyl)-2-methyl-N-phenylpropanamide (**2b**).* White solid, 56.8 mg; 85% yield; mp, 112.9−115.1 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41−7.34 (m, 5H), 7.31−7.23 (m, 3H), 7.08 (m, 1H), 6.75 (s, 1H), 1.65 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.8, 143.1, 137.7, 133.3, 129.1, 128.9, 127.9, 124.3, 123.9, 119.7, 47.7, 27.0. HRMS-ESI (*m*/*z*): calculated for $C_{16}H_{17}ClNO$ (M + H)$^+$, 274.0999; found, 274.0991.

*2-Methyl-N-phenyl-2-(p-tolyl)propanamide (**2c**).* White solid, 61.3 mg; 77% yield; mp, 108.8−112.2 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57−7.49 (m, 2H), 7.41−7.24 (m, 6H), 7.15−7.02 (m, 1H), 6.76 (s, 1H), 1.65 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.7, 143.7, 137.7, 132.0, 128.9, 128.2, 124.3, 121.4, 119.7, 47.7, 26.9. HRMS-ESI (*m*/*z*): calculated for $C_{16}H_{17}{}^{79}BrNO$ (M + H)$^+$, 318.0494; found, 318.0496.

*2-Methyl-N-phenyl-2-(p-tolyl)propanamide (**2d**).* White solid, 35.5 mg; 56% yield; mp, 85.5−86.1 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36−7.32 (m, 4H), 7.27−7.17 (m, 4H), 7.04 (m, 1H), 6.84 (s, 1H), 2.36 (s, 3H),1.64 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.8, 141.4, 137.9, 137.0, 129.6, 128.8, 126.4, 124.0, 119.5, 47.6, 27.0, 21.0. HRMS-ESI (*m*/*z*): calculated for $C_{17}H_{20}NO$ (M + H)$^+$, 254.1545; found, 254.1525.

*2-Methyl-N-phenyl-2-(4-(trifluoromethyl)phenyl)propanamide (**2e**).* White solid, 22.3 mg; 29% yield; mp, 117.5−119.6 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 6.74 (s, 1H). 1.69 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 174.4, 148.8, 137.6, 129.6 (q, *J* = 32.4 Hz), 126.8, 125.9 (q, *J* = 3.7 Hz), 124.4, 123.9 (t, *J* = 136.1 Hz), 119.8, 48.1, 27.0. HRMS-ESI (*m*/*z*): calculated for $C_{17}H_{17}F_3NO$ (M + H)$^+$, 308.1262; found, 308.1252.

*2-(4-Methoxyphenyl)-2-methyl-N-phenylpropanamide (**2f**).* Pale-yellow solid, 22.2 mg; 33% yield; mp, 83.2−84.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39−7.33 (m, 4H), 7.29−7.22 (m, 2H), 7.07−7.03 (m, 1H), 6.98−6.90 (m, 2H), 6.85 (s, 1H), 3.83 (s, 3H), 1.64 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.9, 158.7, 137.9, 136.4, 128.8, 127.6, 124.0, 119.5, 114.2, 55.3, 47.3, 27.1. HRMS-ESI (*m*/*z*): calculated for $C_{17}H_{20}NO_2$ (M + H)$^+$, 270.1494; found, 270.1471.

*2-Methyl-N-phenyl-2-(o-tolyl)propanamide (**2g**).* White solid, 62.7 mg; 99% yield; mp, 95.6−98.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.51−7.49 (m, 1H), 7.36−7.34 (m, 2H), 7.32−7.18 (m, 6H), 7.11−7.03 (m, 1H), 6.85 (s, 1H), 2.31 (s, 3H), 1.66 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.2, 138.8, 137.1, 134.6, 133.7, 132.4, 132.0, 131.7, 130.5, 129.1, 126.1, 58.4, 32.4, 20.8. HRMS-ESI (*m*/*z*): calculated for $C_{17}H_{20}NO$ (M + H)$^+$, 254.1545; found, 254.1543.

*2-Methyl-N-phenyl-2-(m-tolyl)propanamide (**2h**).* White solid, 45.2 mg; 76% yield; mp, 109.9−112.2 °C ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.22 (m, 7H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.06 (td, *J* = 7.2, 0.8 Hz, 1H), 6.83 (s, 1H), 2.39 (s, 3H), 1.66 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.7, 144.4, 138.6, 138.0, 128.8, 128.1, 127.2, 124.0, 123.4, 119.6, 47.9, 27.0, 21.6. HRMS-ESI (*m*/*z*): calculated for $C_{17}H_{20}NO$ (M + H)$^+$, 254.1545; found, 254.1540.

*N,2-Diphenylpropanamide (**2i**):*[19] White solid, 19.0 mg; 34% yield; mp, 114.9−116.3 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47−7.21 (m, 1H), 7.17 (s, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 3.72 (q, *J* = 6.8 Hz, 1H), 1.69 (d, *J* = 7.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.6, 144.2, 137.0, 131.8, 129.1, 127.5, 126.4, 121.2, 116.6, 48.1, 26.9.

*2,2-Difluoro-N,2-diphenylacetamide (**2k**):*[20] White solid, 16.1 mg; 26% yield; mp, 86.6−89.7 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.54−7.44 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ −24.68. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.8 (t, *J* = 31.0 Hz), 136.0, 132.6 (t, *J* = 25.4 Hz), 131.1, 129.2, 128.7, 125.61, 125.58 (t, *J* = 6.1 Hz), 120.1, 114.8 (t, *J* = 254.1 Hz). HRMS-ESI (*m*/*z*): calculated for $C_{14}H_{12}F_2NO$ (M + H)$^+$, 248.0887; found, 248.0885.

*2-Methyl-N-phenyl-2-(thiophen-2-yl)propanamide (**2m**).* White solid, 35.3 mg; 76% yield; mp, 78.1−80.0 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.23 (m, 5H), 7.19 (s, 1H), 7.09 (m, 3H), 1.75 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.3, 149.7, 138.0, 129.1, 127.6, 125.6, 125.2, 124.5, 119.9, 46.5, 28.4. HRMS-ESI (*m*/*z*): calculated for $C_{14}H_{16}NOS$ (M + H)$^+$, 246.0953; found, 246.0953.

*N-(4-Methoxyphenyl)-2-methyl-2-phenylpropanamide (**2n**).* White solid, 54.5 mg; 81% yield; mp, 134.3−136.3 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47−7.38 (m, 4H), 7.35−7.22 (m, 3H), 6.85−6.77 (m, 2H), 6.69 (s, 1H), 3.76 (s, 3H), 1.66 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.4, 156.2, 144.7, 131.0, 128.8, 127.2, 126.4, 121.5, 113.9, 55.4, 47.7, 27.0. HRMS-ESI (*m*/*z*): calculated for $C_{17}H_{20}NO_2$ (M + H)$^+$, 270.1494; found, 270.1473.

*2-Methyl-2-phenyl-N-(p-tolyl)propanamide (**2o**).* White solid, 51.3 mg; 81% yield; mp, 103.8−105.2 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47−7.35 (m, 4H), 7.35−7.28 (m, 1H), 7.25−7.22 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.74 (s, 1H), 2.27 (s, 3H), 1.66 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.4, 144.6, 135.4, 133.7, 129.3, 128.9, 127.3, 126.5, 119.6, 47.9, 27.0, 20.8. HRMS-ESI (*m*/*z*): calculated for $C_{17}H_{20}NO$ (M + H)$^+$, 254.1545; found, 254.1546.

*N-(4-Bromophenyl)-2-methyl-2-phenylpropanamide (**2p**).* White solid, 46.1 mg; 58% yield; mp, 136.2−139.0 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46−7.30 (m, 7H), 7.29−7.22 (m, 2H), 6.79 (s, 1H), 1.66 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.6, 144.2, 137.0, 131.8, 129.1, 127.5, 126.4, 121.2, 116.6, 48.1, 26.9. HRMS-ESI (*m*/*z*): calculated for $C_{16}H_{17}{}^{79}BrNO$ (M + H)$^+$, 318.0494; found, 318.0473.

*N-(4-Chlorophenyl)-2-methyl-2-phenylpropanamide (**2q**).* White solid, 46.5 mg; 68% yield; mp, 133.6−135.1 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47−7.28 (m, 7H), 7.24−7.18 (m, 2H), 6.76 (s, 1H), 1.66 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.6, 144.2, 136.5, 129.0, 128.8, 127.5, 126.4, 120.9, 48.0, 26.9. HRMS-ESI (m/z): calculated for $C_{16}H_{17}ClNO$ $(M + H)^+$, 274.0999; found, 274.0991.

2-Methyl-2-phenyl-N-(4-(trifluoromethyl)phenyl)propanamide ***(2r)***. White solid, 54.5 mg; 71% yield; mp, 104.2−105.9 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55−7.39 (m, 8H), 7.37−7.34 (m, 1H), 6.90 (s, 1H), 1.68 (s, 6H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 175.9, 144.1, 141.0, 129.1, 127.6, 126.4, 126.1 (q, J = 3.7 Hz), 125.8 (q, J = 32.6 Hz), 124.0 (q, J = 269.8 Hz), 119.1, 48.2, 26.9. HRMS-ESI (m/z): calculated for $C_{17}H_{17}F_3NO$ $(M + H)^+$, 308.1262; found, 308.1259.

2-Methyl-2-phenyl-N-(o-tolyl)propanamide ***(2s)***. White solid, 50.0 mg; 79% yield; mp, 87.0−88.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.0 Hz, 1H), 7.54−7.47 (m, 2H), 7.46−7.38 (m, 2H), 7.36−7.30 (m, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.01 (m, 2H), 6.70 (s, 1H), 1.78 (s, 3H), 1.70 (s, 6H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 175.6, 144.6, 135.8, 130.2, 129.0, 127.4, 126.7, 126.6, 124.5, 121.7, 48.0, 26.8, 16.9. HRMS-ESI (m/z): calculated for $C_{17}H_{20}NO$ $(M + H)^+$, 254.1545; found, 254.1542.

2-Methyl-2-phenyl-N-(m-tolyl)propanamide ***(2t)***. White solid, 50.1 mg; 79% yield; mp, 86.6−89.7 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.47−7.37 (m, 4H), 7.34−7.30 (m, 1H), 7.28−7.23 (m, 1H), 7.18−7.08 (m, 2H), 6.87 (m, 1H), 6.76 (s, 1H), 2.29 (s, 3H), 1.66 (s, 6H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 175.5, 144.5, 138.8, 137.8, 129.0, 128.6, 127.3, 126.4, 124.9, 120.2, 116.6, 48.0, 27.0, 21.4. HRMS-ESI (m/z): calculated for $C_{17}H_{20}NO$ $(M + H)^+$, 254.1545; found, 254.1549.

N-(3,5-Dimethylphenyl)-2-methyl-2-phenylpropanamide ***(2u)***. White solid, 47.5 mg; 71% yield; mp, 132.0−133.8 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46−7.37 (m, 4H), 7.32 (m, 1H), 7.00 (s, 2H), 6.70 (s, 2H), 2.24 (s, 6H), 1.65 (s, 6H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 175.5, 144.5, 138.6, 137.7, 128.9, 127.3, 126.4, 125.8, 117.2, 49.2, 48.0, 44.7, 27.0, 21.3. HRMS-ESI (m/z): calculated for $C_{18}H_{22}NO$ $(M + H)^+$, 268.1701; found, 268.1698.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00735.

fac-Ir(ppy)$_3$-catalyzed intramolecular migration reaction and NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interest.

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